National Bureau of Standards

TECHNICAL NEWS BULLETIN

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Viscosimetry of Gases *at High Temperatures and Pressures*

TO PROVIDE data needed for the design of gas turbines and jet engines, the National Bureau of Standards is conducting a broad program of research on the viscosity of gases at elevated temperatures and pressures. Hydrocarbon mixtures and combustion products composed of various proportions of nitrogen, carbon dioxide, argon, oxygen, carbon monoxide, and water vapor are being studied by NBS under the sponsorship of the National Advisory Committee for Aeronautics. In the course of this work, J. C. Westmoreland of the NBS mechanics division staff has developed a unique type of flowmeter which accurately controls and measures the flow of very small volumes of gas, such as those required in a small capillary tube viscometer. As a result, it has been possible to obtain hitherto unavailable data on the viscosity of pure gases and their mixtures.

Accurate data on the viscosity of gases are required in design of transmission and measurement systems for fuel gases and in construction of gas-flow systems in chemical plants. Because the viscosity of a gas is an important factor in the rate of heat transmission between gases and metals, gas-viscosity data are also needed in the design of gas turbines and jet engines. With the continued development of new engines of this kind, the need for information on the viscosity of the exhaust gases at high temperatures is becoming increasingly important.

At present, available data on the viscosity of gases are very meager, particularly at temperatures above 1,000° F. To meet this need, the Bureau has undertaken to determine the viscosity of pure gases and gas mixtures at pressures from 5 to 10,000 lb/in^2 and over the temperature range from 60° to 2,500° F.

In the NBS program, viscosities are measured by timing the flow of the gas under study through a very fine capillary tube. If the dimensions of the tube are known, the viscosity can be computed by means of Poiseuille's law [1] from the volume rate of flow through the tube and the pressure drop from inlet to outlet of the tube. The capillary tubes are of Inconel, with average internal bores of 0.038 cm and lengths up to 434 cm. For high-pressure operation the tubes are enclosed so that they have only to withstand the small pressure differential caused by the flow of gas. The capillary enclosure is heated electrically, and temperatures are measured with chromel-alumel thermocouples. At high temperatures a coiled capillary is used.

In order to obtain as accurate viscosity values as possible, the Bureau decided to measure the rate of flow of the gas through the capillaries by means of some metering device employing a volumetric displacement. This method would have the advantage that the volume could be evaluated directly by conventional methods and would not involve the measurement of an auxiliary

[1] According to Poiseuille's law, when a fluid flows through a capillary tube, the volume rate of flow is given by $\pi r^4 \Delta p/8\eta l$ where r is the radius and l the length of the capillary, Δp is the pressure drop across the tube, and η is the coefficient of viscosity of the fluid.

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quantity. As no flowmeter capable of measuring the extremely small flow rates through the tubes was available, it was necessary to design such an instrument. The apparatus that was developed not only determines these flow rates accurately at pressures up to 500 atmospheres but also includes a means of regulating the rate of flow and of measuring or pre-establishing the pressure drop over the capillary.

In previous investigations determination of the viscosity of a gas at high pressures has required a knowledge of the compressibility effects of the particular gas being tested. However, in the NBS experiments the new flowmeter is used to measure the volume rate of gas flow at the static pressure of the test, and an absolute knowledge of the compressibility of the gas may not be required. Under the conditions of operation of this device, the Poiseuille expression is completely defined at the test pressure and temperature, and the relationship is essentially independent of the thermodynamic deviations from an ideal gas.[2]

The flowmeter developed at the Bureau consists essentially of a calibrated volume chamber, a float-valve chamber, and a gas-mercury reservoir. These are connected in with the calibrated capillary tube to form a closed system in which the gas under study flows out of the reservoir and through the capillary tube to displace mercury in the volume chamber. The float valve regulates the flow of mercury out of the volume chamber as it is displaced by the incoming gas and at the same time maintains constant the height of a mercury column which provides a hydrostatic pressure causing the gas to flow through the capillary tube. As the mercury passes out of the volume chamber, it breaks electrical contact with successive platinum electrodes, activating

[2] The compressibility of a gas is not independent of temperature; and if the flowmeter cannot be operated at the same temperature and pressure as the capillary tube, it will, of course, be necessary to make the appropriate correction to the volume.

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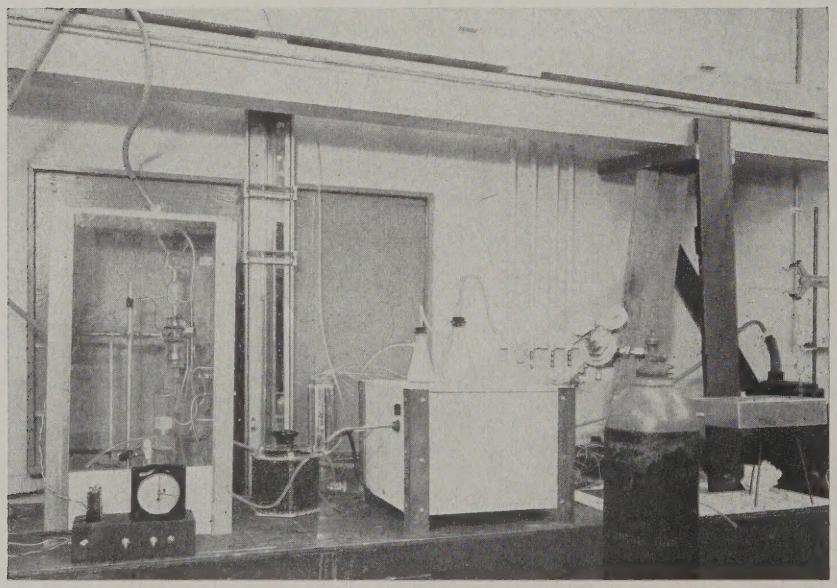
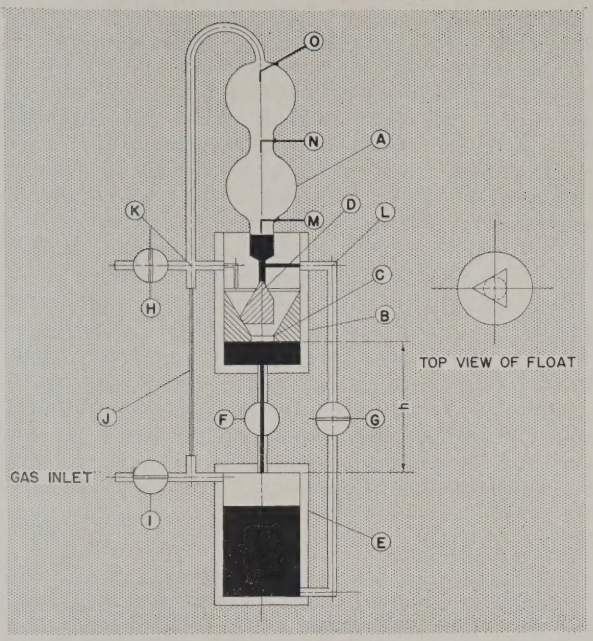


Apparatus used at the Bureau in studies of the viscosity of jet combustion gases at high temperatures. Viscosity is determined by measurement of the rate of flow of the gas under study through a very fine coiled capillary tube within the high-temperature furnace (center). All of the gas which flows through the capillary tube also passes through the new NBS flowmeter (enclosed in the transparent temperature-controlled enclosure at left), where the time for a given volume to flow through the capillary is measured and indicated on the clock in front of the meter. The gas sample, obtained from the gas cylinder at right, flows first through flasks (above furnace) containing a drying agent before entering the capillary in the high-temperature furnace. The manometers (right of flowmeter) measure the vacuum within the flowmeter.



Schematic diagram of the new flowmeter developed for measuring the rate of flow of very small volumes of gas through capillary tubes. The capillary tube (J) is connected into the meter to form a closed system in which the gas under study flows out of a reservoir (E) and through the capillary tube to displace mercury in the calibrated volume chamber (A). The float valve (D) regulates the flow of mercury out of the volume chamber as it is displaced by the incoming gas and also maintains constant the height (h) of the mercury column which supplies the hydrostatic pressure causing the gas to flow through the capillary tube. As the displaced mercury passes out of the calibrated volume chamber, it breaks contact successively with the electrodes O, N, and M, thus activating a timing circuit. The pressure in the float-valve chamber is made equal to that in the calibrated volume chamber by the connecting tube K. The valve H connects the apparatus to a vacuum system for preliminary purging of gas. The gas sample to be studied is admitted to the flowmeter through the valve I. The tube L and valves F and G are used in filling the reservoir (E) with gas and the volume chamber with mercury before measurements are begun.

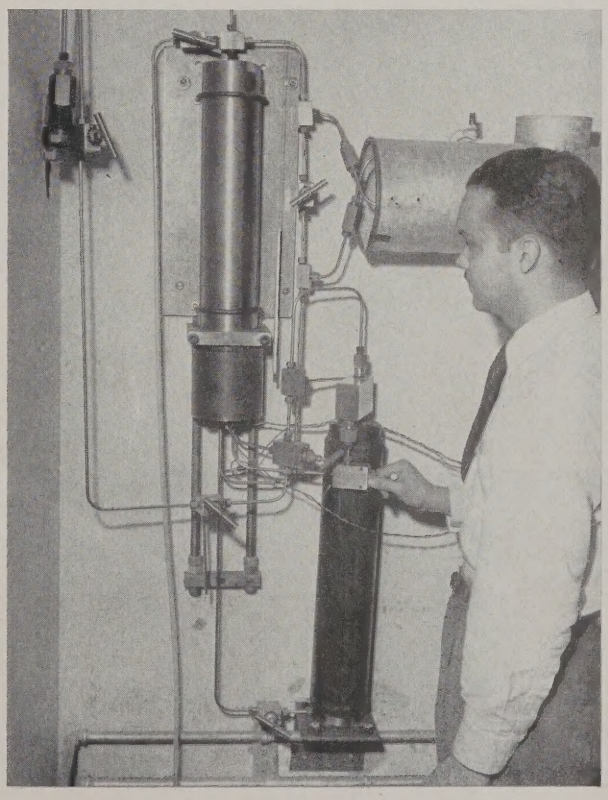
relays which start and stop a clock. In this way the time required for the measured volume of gas to flow through the capillary tube is ascertained.

No energy from the gas stream is employed in replacing the mercury, which is made to flow by gravity out of the calibrated container through the float valve chamber at a rate equal to the rate of gas inflow. The replaced mercury is then added to the top of the mercury in the hydrostatic column, replacing mercury which passes out of the small-diameter tube forming the power part of the column and into the gas-mercury reservoir. The mercury which thus enters the reservoir in turn replaces the gas which is continually leaving the reservoir to pass through the calibrated capillary tube. A pressure-equalization tube which joins the calibrated gas collection chamber to the float valve chamber insures that the pressure differential across the capillary tube is only that due to the column of mercury above the gas-mercury reservoir.

The volume chamber, made of glass, is divided into two equal parts, one above the other, with a necked section in between the two and at the base of the lower chamber. The principal purpose of the upper volume is to provide a starting period during which flow conditions may become stabilized. The necked sections make the cross-sectional area small in the plane of the contact break.

The float chamber, float, and valve are all made of methyl methacrylate. A valve and valve seat of this plastic material are not eroded by the flowing mercury as a steel valve would be. Moreover, the mercury remains clean in contact with the methyl methacrylate.

In the operation of the flowmeter the entire apparatus, with all of the mercury in the reservoir, is first connected to a high-vacuum pump and purged of gas as completely as possible. A valve in the column between the float-valve chamber and the gas-mercury reservoir is then closed, and a gas-sample inlet valve is opened, admitting gas from an external container to the reservoir. This causes the mercury in the reservoir to rise through an auxiliary connecting tube into the passage



Apparatus developed by NBS for study of the viscosity of gases at high pressures. A pressurized model of the new NBS flowmeter (within the two cylinders at left) is used to measure the rate of flow of the gas under study through a very fine calibrated capillary tube enclosed in the insulated and heated enclosure at upper right. The pressurized container at upper left contains all of the flowmeter except the gas-mercury reservoir, which is in the pressurized container below and to the right of the other.

above the float valve. As the tube below the float valve is now blocked off, the mercury will first fill the float chamber enough to close the float valve and will then fill the calibrated volume chamber. A cock in the auxiliary connecting tube is then closed. When the inflow of the sample gas has brought the pressure within the reservoir to the desired value, the gas sample inlet valve is also closed.

Before measurements are taken, sufficient time must elapse for pressure conditions to equalize throughout the system. Then the meter is placed in operation by opening the valve in the column connecting the float-valve chamber with the gas-mercury reservoir. The outflow of mercury from the float-valve chamber lowers the float, opening the float valve so as to admit mercury from the calibrated volume container into the float-valve chamber. Whenever this inflow from the volume chamber exceeds the outflow into the reservoir, the float valve automatically closes. Thus the pressure which the mercury column exerts on the gas entering the capillary tube is kept constant, and the rate at which mercury flows out of the volume chamber is controlled by the rate of flow of gas through the capillary.

In making the determinations, the apparatus is first pressurized at a specific temperature. Flow measurements are then carried out at decreasing pressure levels, and the viscosities are computed for each value of pressure. This procedure gives a family of isotherms showing the variation in the viscosity of the gas sample with pressure at the temperature of the test.

In addition to being used in viscosity studies, the new flowmeter may find application in the determination of the specific gravity of a gas by the effusion method. For this purpose the capillary tube would be replaced by a thin metal diaphragm containing a small orifice.

Because the viscosity of a gas changes rapidly with temperature, the Bureau's flowmeter should also prove useful for measuring temperatures, particularly at elevated levels where thermoelectric means have proved unreliable. For such use, the capillary tube would be coiled into a compact sensing unit that would be charged once and for all with a suitable gas. The time interval for a given volume of the gas to flow through the capillary would then be a measure of the average temperature of the capillary.

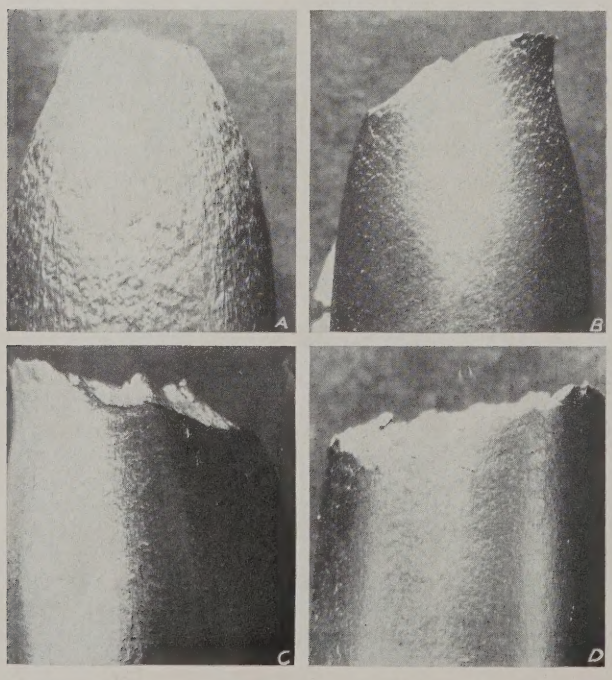
For further technical details, see A meter for timing the flow of very small volumes of a gas, *by J. C. Westmoreland, NACA Research Memorandum RM52109.*

Tensile Properties of Copper

THE BUREAU has recently completed a study of the effect of prior strain history on the room-temperature tensile properties and microstructure of high-purity copper. Tensile tests were made on oxygen-free high-conductivity (OFHC) copper initially as annealed, as cold-drawn different amounts, and as prestrained in creep at 110°, 250°, and 300° F. The results show that the strength, ductility, and hardness of the copper are markedly affected by its prior strain history. The investigation was conducted by William D. Jenkins and Thomas G. Digges of the NBS thermal metallurgy laboratory.

Considerable interest has been stimulated among metallurgists by suggestions that the tensile properties of metals are dependent only upon the instantaneous strain state of the metal and are practically independent of the manner in which this state is attained. Previous NBS work has shown, however, that as some metals and alloys are deformed, hardening and recovery occur in such a manner that subsequent tensile properties are materially affected.

Four bars of OFHC copper, 99.99 plus percent pure, were procured for the NBS study. All had been processed from the same lot of copper, but each had



Photographs of representative copper specimens showing surface conditions after fracture. Unetched, Magnification: × 3⅔.

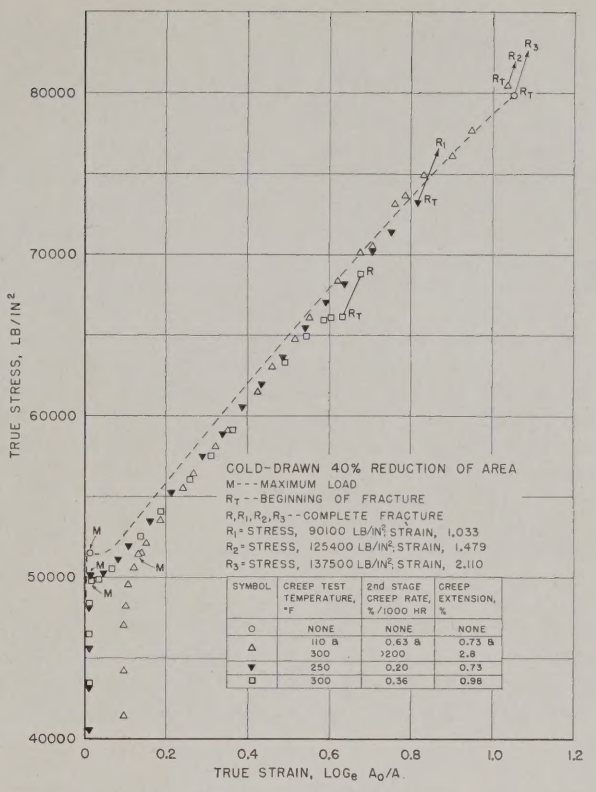
	Initial condition	Creep test			Remarks
		Temperature	Rate	Plastic extension	
		°F	%/1,000 hr		
A	Cold-drawn 70% reduction of area; annealed 1,300° F.	None	None	None	Fractured at room temperature.
B	Annealed 800° F	250	1.04	23.1	Do.
C	Cold-drawn 40% reduction of area.	300	.36	.98	Do.
D	Annealed 800° F	300	8.3	36.5	Fractured in creep at 300° F.

been subjected to different conditions of annealing or cold drawing. Specimens taken from the various bars were subjected at the Bureau to different amounts of prestraining in creep under tension at 110°, 250°, or 300° F. The differently preconditioned specimens were then all tested in tension at room temperature at the same rate of extension of 1 percent per minute.

Cold-drawing the copper at a relatively fast strain rate generally resulted in increased strength and hardness but in decreased ductility (as measured by the extension and reduction of area at fracture). Prestraining at a high temperature or at a low strain rate, on the other hand, generally resulted in reduced strength and hardness as well as reduced ductility. Specimens with the larger grain sizes showed lower yield strengths and hardness values; but grain size had very little effect on tensile strength, fracture strength, and ductility. Hardness values of the fractured tensile specimens, obtained at room temperature, confirmed the results of the tensile tests.

The microstructures of the tensile specimens were, in general, consistent with previous assumptions that cracks of a transcrystalline nature, and substructures, are nucleated during the second stage of creep, and that these phenomena are associated with prestraining at low temperatures and fast strain rates. Cracks thus nucleated grew to microscopic dimensions during the tensile tests. Prestraining at elevated temperatures and slow strain rates tended to result in fractures of a less ductile type and in cracks of an intercrystalline nature.

For further technical details, see Influence of prior strain history on the tensile properties and structures of high-purity copper, *by William D. Jenkins and Thomas G. Digges, J. Research NBS* **49,** *167 (Sept. 1952); reprinted as NBS Research Paper 2354, obtainable for 15 cents from Superintendent of Documents, Government Printing Office, Washington 25, D. C.*



NBS data showing effect of prestraining in creep on the true stress-strain relation, at room temperature, of high-purity oxygen-free high-conductivity copper prestrained 40-percent reduction of area. Specimens were tested in tension at room temperature at a rate of extension of 1 percent per minute. Average grain diameter before cold-drawing was 0.025 millimeter. The NBS study was made to determine the effects of different prestraining on the tensile properties, hardness, and microstructure of high-purity copper.

Mixing Silicate Cement

A film demonstrating a new method of mixing silicate cement in a closed container has recently been produced by the National Bureau of Standards and the Council on Dental Research of the American Dental Association. In this method the maximum amount of powder is incorporated into a given quantity of liquid independent of atmospheric conditions. Differences in properties of silicate cement when mixed under summer and winter conditions indicate the great effect of variations in temperature and humidity of the air. Actual restorations in the mouth show how these research laboratory findings may be demonstrated in dental practice.

A Method of Mixing Dental Cement, a 16-mm. color and sound film, runs for 8 minutes. It may be obtained on loan. Also, it may be purchased for $40.31.[1]

Four other technical films on dental practices and techniques are available for loan or purchase. They are 16-mm sound and color films, each running approximately 18 minutes. *Silicate Cement* (purchase price,[1] $81.42) demonstrates the effect of technique on such critical cement properties as setting time, strength, shrinkage, solubility, and staining. *Dental Amalgam: Failure Caused by Moisture Contamination* (purchase price,[1] $62.23) describes a satisfactory technique for the prevention of one of the most common causes of amalgam failure. *Denture Resin* (purchase price,[1] $80.72) shows the effect of impurities, pressure, temperature, rate of curing, duration of curing, mold surfaces, and water content on the dimensional accuracy and stability of dentures made from acrylic resins. *The Casting of Dental Gold Alloys; Thermal Expansion Technique* (purchase price,[1] $77.44) demonstrates means for the prevention of warpage of wax patterns, selection and attachment of the sprue, investing, elimination of the wax pattern, and melting and casting of the alloy.

These films may be obtained on loan or purchase by application to the Office of Scientific Publications, National Bureau of Standards, Washington 25, D. C., or the American Dental Association, 222 East Superior Street, Chicago 11, Ill.

[1] Purchase prices are subject to change without notice.

Sound Absorption of INSTALLED ACOUSTIC MATERIALS

TO MEASURE the effectiveness of newly installed or redecorated acoustic materials the National Bureau of Standards has recently developed a "long-tube method." Devised by Earle Jones, Seymour Edelman, and Albert London of the NBS sound laboratory, the method, which determines the sound-absorption coefficient of materials without defacing them, provides distinct advantages over attempts at laboratory evaluation of such materials. Field measurements of the installed acoustic materials will not only give a check on compliance with specifications but also will permit the examination of a small portion of the material before and after use of a particular means of redecoration.

Acoustic materials installed in a building may have sound-absorption coefficients that vary considerably from those indicated by careful laboratory tests. As a result, the installation may fail to comply with specifications written on the basis of such tests. Laboratory samples of acoustic plasters are constructed under controlled conditions and usually yield repeatable test results, even when tested by different laboratories. However, when the materials are installed, the sound-absorption properties depend to a large degree on such factors as the care devoted to the mixing of the ingredients, the skill of the plasterer, and the conditions under which the plaster is cured. Also, when this material becomes soiled or otherwise requires redecoration, the choice of a poor method for restoration of its appearance may result in the loss or diminution of its sound absorption properties.

In the NBS long-tube method a standing sound-wave pattern of 500 cycles per second is set up within a tube, one end of which is closed by the acoustic material being tested. The sound-absorption coefficient for normal incidence is computed from measurements of the maximum and minimum pressures in the standing wave pattern. The random incidence absorption coefficient—the value that corresponds to the value that would be determined by a reverberation-room test—is determined from the normal incidence coefficient by a calculation based on semiempirical considerations.[1]

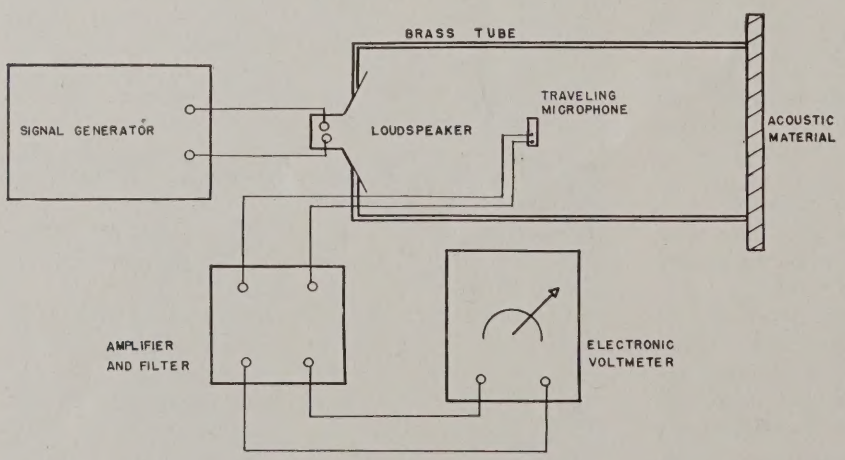
The tube is constructed of 1/8-in. brass tubing, 9¾ in. in diameter and about 30 in. long. The diameter of the tube was chosen so that the cutoff frequency of the first transverse mode—700 cps—was well above the frequency at measurement. This diameter permits measurements on large samples and also reduces the effects of the attenuation due to the walls of the tube. Thus, the tube is long enough to allow at least two minima and one maximum to be found but not too long for easy handling. The tube is pivoted so that it can be used at any angle between vertical and horizontal. The pivot supports, on a jackscrew, permit the tube to be moved vertically about one foot. The entire mount moves easily on casters from place to place.

The sound source is a 6-in. permanent-magnet speaker mounted on a 1/8-in. brass plate covering the back of the tube. Of the several types of microphones tried, the most successful was a hearing-aid-type crystal microphone, which is mounted on the center bar of a metal H-shaped member. This assembly rolls on a track which permits the positioning of the microphone at any point throughout the length of the tube.

A bakelite housing cemented over the magnetic pot of the loudspeaker shields the back of the tube from extraneous sound. After much experimentation, it was found that a caulking-compound gasket would bond the tube to the material being tested without too much leakage of sound and without damage to the material.

Simulated field measurements were made on three different samples of some 50 acoustic materials pre-

[1] *For an explanation of this calculation, see* Determination of reverberant sound-absorption coefficients from acoustic impedance measurements, *by Dr. Albert London, J. Acous. Soc. Am.* **22**, *263 (1950).*



Block diagram of tube and associated equipment as used in field measurements of sound-absorption coefficient. The tube is constructed of 1/8-in. brass tubing, 9¾ in. in diameter and about 30 in. long. The tube is long enough to allow at least two minima and one maximum to be found but not too long for easy handling. It is pivoted so that it can be used at any angle between vertical and horizontal. The pivot supports, on a jackscrew, permit the tube to be moved vertically about one foot. The entire amount moves easily on casters from place to place. The sound source is a 6-in. permanent-magnet speaker mounted on a 1/8-in. brass plate covering the back of the tube. The signal from an oscillator drives the loudspeaker.

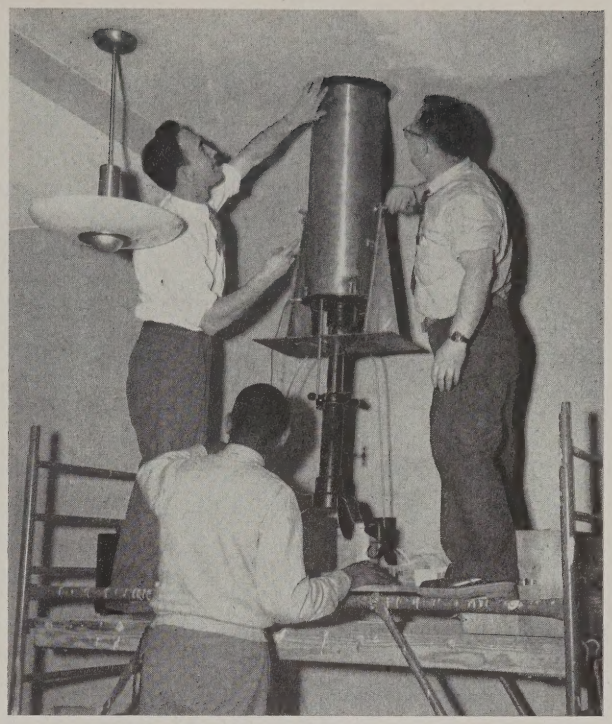
viously tested in the Bureau's reverberation chamber. Each specimen was tested three times. The corrected deviations of the tube measurements from the reverberation-chamber measurements ranged from +0.18 to −0.21. The average of the absolute values of these deviations was 0.05, and 70 percent of all of the deviations fell between +0.05 and −0.05.

The samples used for the simulated field measurements included many types of prefabricated acoustic materials. No correlation could be found between the amount of the deviation and the type of surface of the acoustic tile or between the amount of the deviation and the thickness of the tile. If the samples used for simulated field tests are a fair representation of all acoustic materials, it appears that the coefficient found by means of the tube method will be within ±0.05 of the coefficient found in the reverberation chamber about 70 percent of the time and within ±0.10 about 80 percent of the time.

NBS found in a series of measurements made on acoustic plaster that the absorption coefficient varies from point to point by considerable amounts and that the difference in absorption coefficient is closely correlated with differences in the appearance of the material. On acoustic plaster, therefore, it is important to make measurements at as many different locations as practicable, especially those points having different surface texture. Acoustic tile appears to be more uniform from one sample to another, making fewer measurements necessary.

The availability of a portable apparatus for nondestructive field testing permits correlation of the appearance of a small area of acoustic plaster with its sound-absorption qualities. The sound absorption of the finished plaster is greatly affected by such details of workmanship as the pressure of the trowel on the plaster, time of final troweling after application, consistency of mix, and the texture imparted to the surface by the use of a stiff straw brush or a nail perforator or both. However, it is not known just how plaster should be applied for best results. The development of the long-tube method makes possible objective evaluation of these various factors, allowing measurement of the sound absorption of small areas so that samples of many different examples of workmanship can be taken.

The necessity of avoiding transverse modes sets an upper limit to the frequency at which a tube can be used. The lower limit of usable frequency is set by the requirement that the tube be short enough for easy handling. These limits restrict the use of the tube described here to frequencies near 500 cycles per second, one of the frequencies used in laboratory reverberation testing. However, other experiments indicate that if the formula used in calculation of the absorption coefficient is applied over the range of frequencies from 250 to 2,000 cps, the deviations between the tube method and the reverberation-chamber method tend to be in opposite directions at different frequencies so that the noise coefficient calculated from tube measurements agrees quite well with that calculated from reverberation-chamber measurements.



Test made on a ceiling, demonstrating the use of the field procedure in determination of the sound-absorption coefficient by means of the long-tube method. When the tube is mounted vertically on casters, the top of it can be set at any height from about 5 ft 2 in. to 5 ft 10 in.

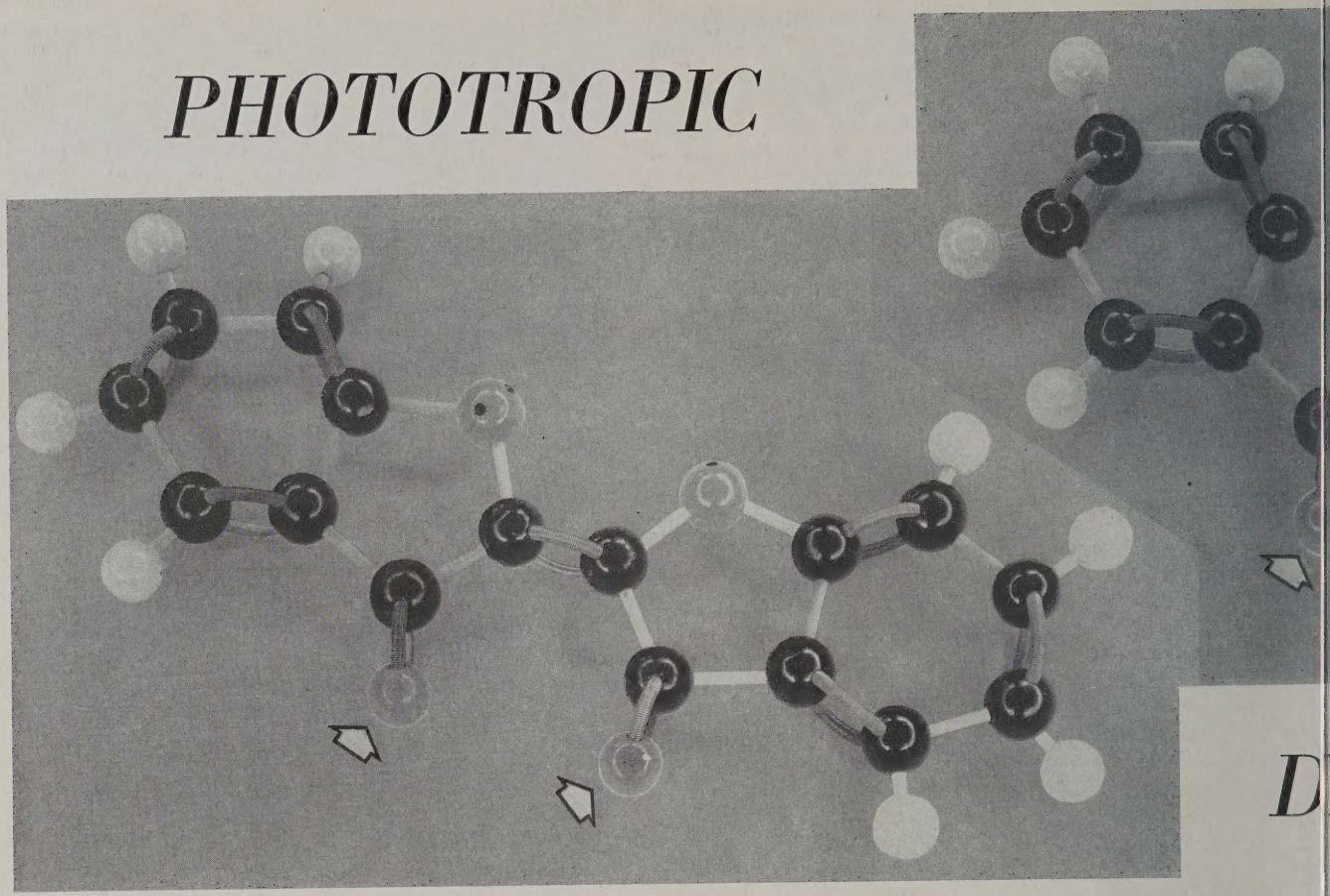
The frequency range from 250 to 2,000 cps could be covered by use of a separate tube of suitable size for each frequency; however, this arrangement would be awkward. On the other hand, it appears possible to replace the long tube with a tube so short as to constitute a cavity. Such a device would be readily portable and should operate over an extended frequency range. A preliminary investigation of this method is in process at the Bureau.

For further technical details, see Long-tube method for field determination of sound-absorption coefficients, *by Earle Jones, Seymour Edelman, and Albert London, J. Research NBS* **49**, *17 (July, 1952); reprinted as NBS Research Paper 2339, obtainable for 5 cents from Superintendent of Documents, Government Printing Office, Washington 25, D. C.*

New Radiation Handbook

Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water, the first official published report of the Subcommittee on Permissible Internal Dose of the National Committee on Radiation Protection, gives the most acceptable values thus far ascertained. It considers those radioisotopes that are of present-day interest. The 45-page report, Handbook 52, may be obtained for 20 cents from the Government Printing Office, Washington 25, D. C.

PHOTOTROPIC



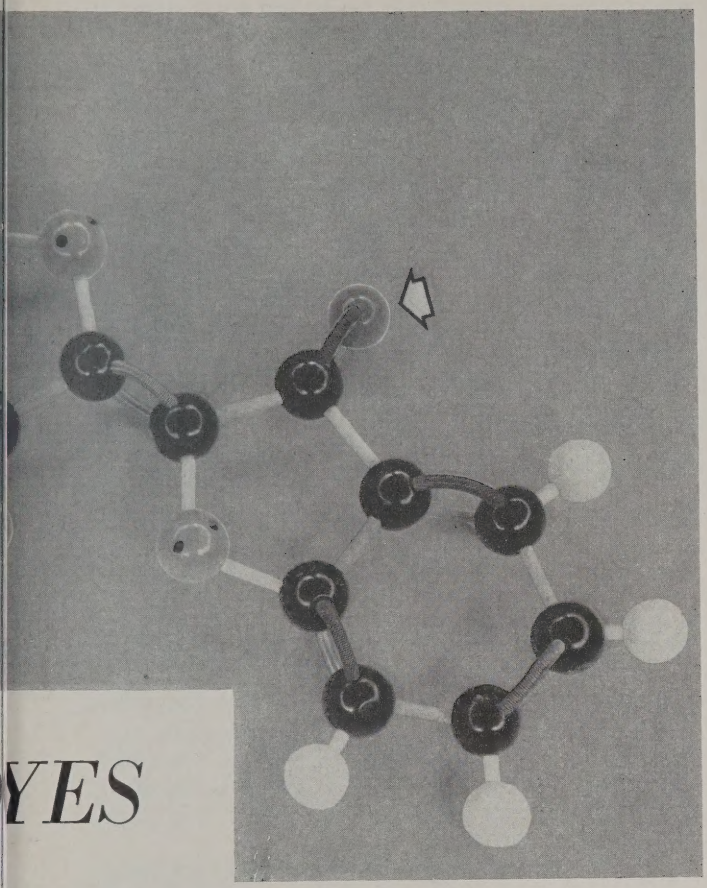
INTERESTING INFORMATION regarding the effects of light on organic dyes has resulted from a program of research which the National Bureau of Standards is conducting on the photochemistry of dyestuffs. Through intensive studies of the absorption spectra of thioindigo and azo dyes, it has been possible to correlate the color changes of light-sensitive dyes with changes in molecular configuration. While the results obtained thus far apply primarily to reversible changes in the color of dyes in solution, they should provide a valuable basis for further studies on the irreversible fading of dyed fabrics during use.

The fading of dyes and dyed fabrics upon exposure to light constitutes an important problem in the dyestuff and textile industries, and considerable effort is now being expended to develop dyes of improved light-fastness. Although the term "fading" ordinarily implies loss of color or reduced intensity, in the field of dyes it may be used to indicate a darkening as well as a lightening of color. Fading involves a change in hue, intensity, brightness, or any combination of these characteristics, which may be detected in the laboratory as a change in the spectral absorption curve of the dye. Because the absorption curve is an inherent characteristic of the dye molecule as a whole, fading must necessarily involve some alteration in the structure or state of aggregation of the dye molecules.

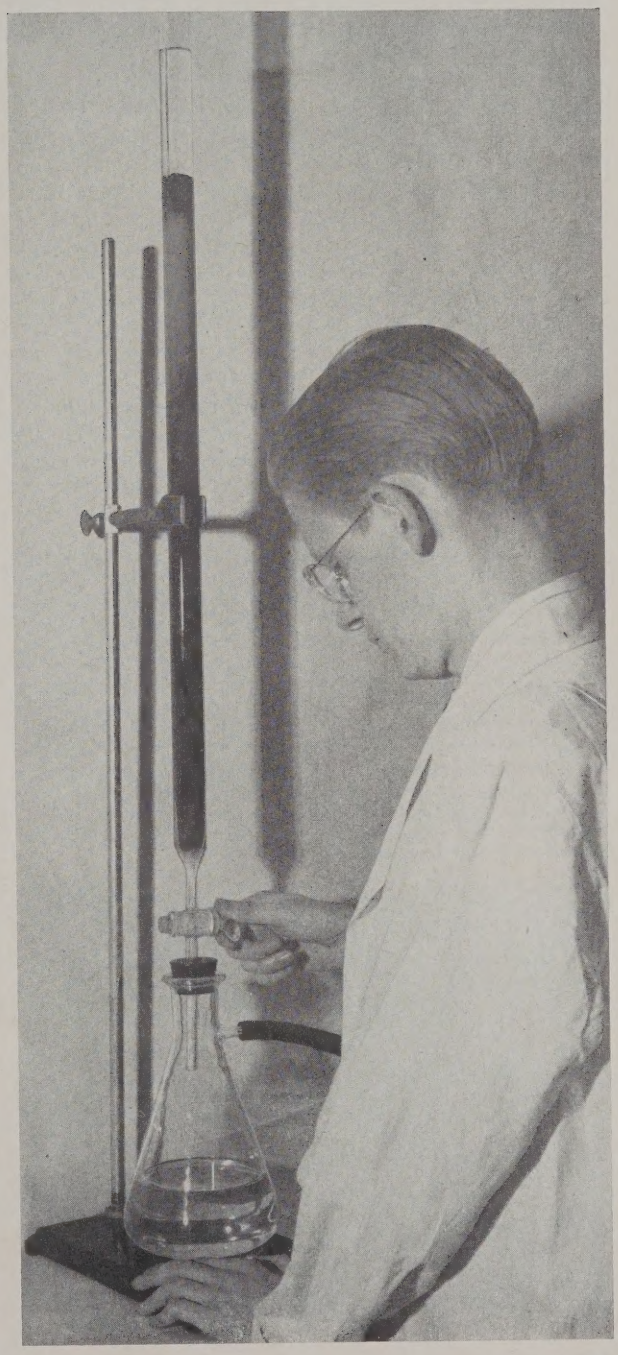
In general, the fading of dyes may be reversible or irreversible, depending on the nature of the chemical changes that cause the change in the absorption spectrum. Those dyes which exhibit reversible changes in their spectra upon irradiation with visible or ultraviolet light are said to be phototropic. The investigation of phototropic dyes is part of a general program in which NBS seeks to determine the effect not only of light but also of heat and other variables on the absorption spectra of various kinds of dyes. This program is being conducted by Dr. G. M. Wyman and J. H. Gould of the NBS staff with the collaboration of Dr. Wallace R. Brode, Associate Director of the Bureau. It is partially supported by the Department of Defense.

The NBS study of phototropic dyes began with an investigation of a number of thioindigo dyes dissolved in benzene or chloroform. It was observed that the absorption spectrum of the solution was not always the same but was dependent on the illumination to which it had been exposed before the measurement. Exposure to light in the wavelength range of the first (longer wavelength) absorption band (yellow or red light, depending on the dye used) led to a reduction in the intensity of this band and the appearance of a new absorption band at a shorter (by about 50 millimicrons) wavelength. This change was readily reversed to yield the original spectrum simply by exposure of the solution to light of a wavelength range corresponding to the new absorption band.

Spectral changes of this kind in the thioindigo dyes are appreciable, and in some instances they may be



Left: Molecular models of *cis* (far left) and *trans* (left) isomers of thioindigo. In *cis* form oxygen atoms (arrows) of carbonyl group are on same side of molecule; in *trans* form they are on diagonally opposite sides. Black spheres represent carbon atoms. *Below:* Chromatographic separation of *cis* and *trans* isomers by selective adsorption in column of silica gel. Adsorbed *cis* isomer appears as narrow dark ring at top of column; *trans* form produces more diffuse dark region beginning a few inches below.

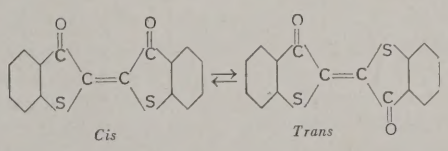


YES

observed visually. For example, the dye known as 6,6′-diethoxythioindigo ordinarily is orange-brown in benzene solution; upon irradiation with orange-yellow light the solution changes to a lemon yellow, which can be reversed to the original orange-brown by irradiation with blue light.

The chemical structure of thioindigo dyes consists of two ring systems connected through a central double bond, each system containing a polar carbonyl (=CO) group. Like other organic compounds containing double bonds, thioindigo dyes can exist as two different space isomers, designated *cis* and *trans*. In the *cis* form the carbonyl groups are on the same side of the molecule while in the *trans* form they are on diagonally opposite sides. Thus, the *trans* isomer has a center of symmetry and for this reason is nonpolar, whereas the *cis* form lacks a center of symmetry and therefore has a dipole moment.

It seemed probable that the phototropic changes that had been observed in the thioindigo dye solutions could



Structural formula of thioindigo.

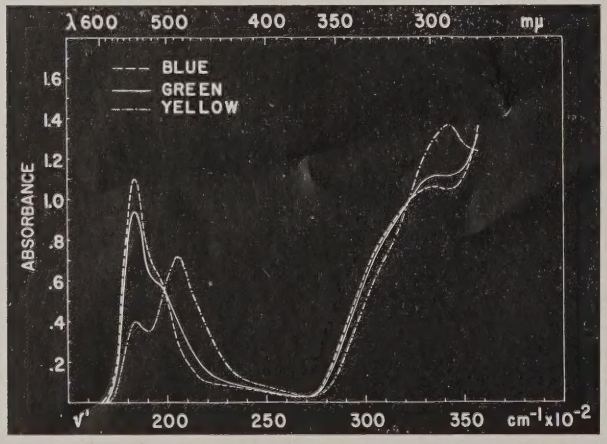
be attributed to a shift in the equilibrium between *cis* and *trans* forms, or in other words, to a photochemical conversion of some molecule of one isomer to the other isomer. Final proof of this theory was obtained when the two isomers of thioindigo were separated by chromatographic adsorption in the absence of light and their absorption spectra were determined.

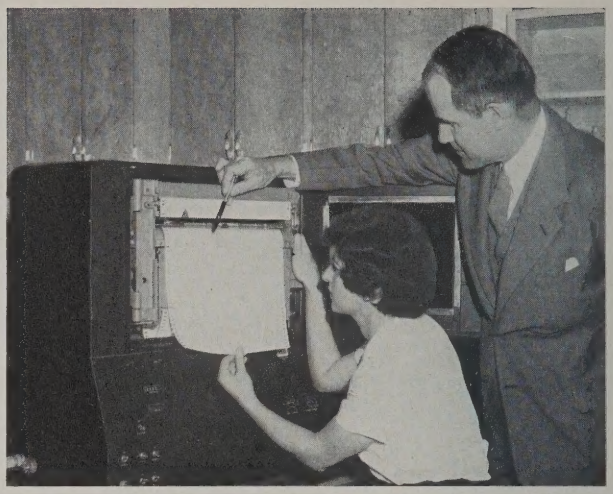
Apparently, in these instances irradiation of one isomer with light of the wavelength range selectively absorbed by that isomer results in partial conversion to the other isomer. Thus, by irradiation with light of the proper wavelength, it is possible to enrich a solution preferentially with respect to either form.

In the NBS experiments, a solution of thioindigo in benzene was first enriched with respect to the *cis* form by exposure to yellow light (about 520 millimicrons) for 20 min. The enriched solution was then poured into a column packed with silica gel. Because the more polar *cis* form is adsorbed more strongly on the adsorbent, the nonpolar *trans* form is more readily removed by washing with a solvent such as benzene. After the two isomers had been separated in this way, their individual absorption spectra were obtained. The entire separation process was carried out in a darkroom, illuminated only by a deep red light of low intensity, which color is not absorbed by either isomer of this particular dye, and the separated isomers were kept in darkness until their spectra were determined.

In benzene solution the *cis* isomer of thioindigo appears orange-colored whereas the *trans* form is pink; their absorption curves are correspondingly different when determined before exposure to light. On standing in daylight the solution containing the *cis* form turns pink gradually, indicating spontaneous conversion to the *trans* isomer; and after a half hour the two solutions are spectrophotometrically indistinguishable, which indicates that equilibrium has been established. Similar results were obtained with other thioindigo compounds.

Effect of irradiation with light of different colors on the absorption spectrum of thioindigo in benzene solution. The spectrum indicated by the dashed line results upon exposure to blue light, the solid-line curve is produced by exposure to green light, and the curve of alternate dots and dashes is obtained when the solution is exposed to yellow light. As may be seen from graph, exposure to yellow light (which is in the wavelength range of the longer-wavelength absorption band in the 550-μ region) leads to a reduction in the intensity of the 550-μ band and the appearance of a new band at about 480 μ. On the other hand, exposure to blue or green light (whose wavelength is in the range of the band at 480 μ) results in the disappearance of this band and the intensification of the band at 550 μ.





Studies of the absorption spectra of thioindigo and azo dyes at the National Bureau of Standards have shown that reversible color changes in these dyes result from a shift in the equilibrium between *cis* and *trans* isomers.

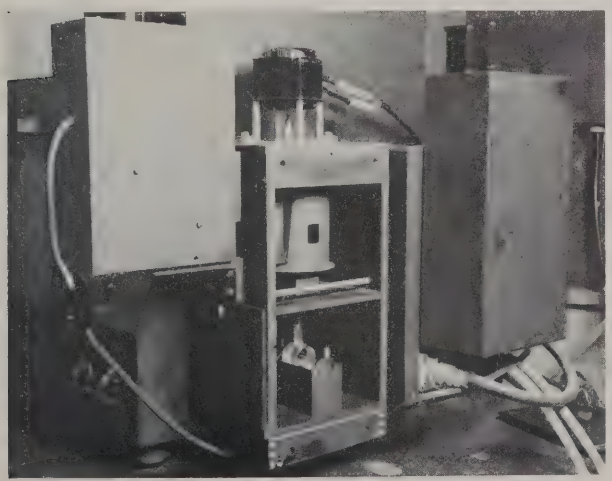
The investigation was then extended to the azo dyes, another important group containing a central double bond. Previously the *cis* and *trans* isomers of azobenzene and some simple azobenzene derivatives had been separated and identified by G. S. Hartley and A. H. Cook in England, and the existence of a photochemical *trans*-to-*cis* conversion in these compounds had been established. However, because in each case the two isomers had similar spectral absorption curves, isomerization resulted in only slight changes in the spectra of the solutions. No direct evidence concerning the existence of *cis* and *trans* isomers of amino or hydroxy azobenzenes could be obtained by these investigators. About ten years ago E. I. Stearns noted that dimethylamino azobenzene (along with a large number of dyes of varied structures) shows a rapid change in color upon exposure to intense light, followed by speedy reversal to the original color in darkness; but no attempt was made to correlate this phototropic behavior with changes in chemical structure

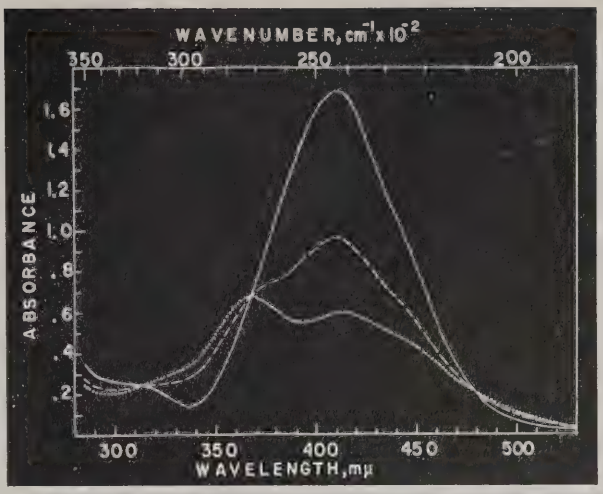
At the National Bureau of Standards, a preliminary study of several 4-amino azobenzenes in benzene solution indicated that their absorption spectra are indeed a function of the irradiation to which they have previously been exposed. However, the reversal of this phototropic change is so rapid that, even during the 3 to 5 minutes required to obtain a complete spectrum on a recording spectrophotometer, the spectra undergo considerable change. It was therefore necessary to design and construct a special shutter device permitting

essentially simultaneous illumination and measurement of the solutions. With the aid of this shutter, it was possible to obtain reproducible absorption curves characteristic of the irradiated solutions.

The phototropic behavior of these azo dyes was found to parallel that of the thioindigo dyes: Upon irradiation with light of a wavelength range corresponding to the principal absorption band of the dye, the intensity of that band is considerably decreased, and a new band appears at a slightly shorter wavelength. However, immediately following removal of the irradiation the absorption curve changes back rapidly, especially when the solution is stored in the absence of light. This rapid reversal in the absence of irradiation constitutes the principal difference between the behavior of the azo dyes and that of the thioindigo dyes. Thus, it seems likely that solutions of the azo dyes under normal laboratory illumination contain both *cis* and *trans* isomers in equilibrium, with the formation of the former favored by irradiation within a wavelength range absorbed by the latter. The *cis* isomers of these azo compounds apparently are much less stable (relative to their *trans* counterparts) than in the case of thioindigo dyes, and for this reason it is believed to be impossible to separate the two geometrical isomers of amino- or hydroxy-substituted azo compounds. It is possible, however, to calculate the approximate spectral absorption curves of the two forms from the curves obtained under different conditions of illumination.

The special shutter device developed for study of very rapid phototropic changes in azo dyes is shown installed (in the compartment just below the small electric motor) in a spectrophotometer. The device consists of two concentric cylinders, both open at the bottom, which are placed over the sample absorption cell in the sample compartment. The outer, stationary cylinder is attached to the cover of the sample compartment; the inner cylinder is driven by the synchronous motor above. The openings in the cylinders are so arranged that the sample is alternately illuminated first by an exciting light beam and then by the monochromator beam of the spectrophotometer for very short intervals of time. In this way, practically instantaneous excitation and measurement of rapidly reversed phototropic changes are obtained.



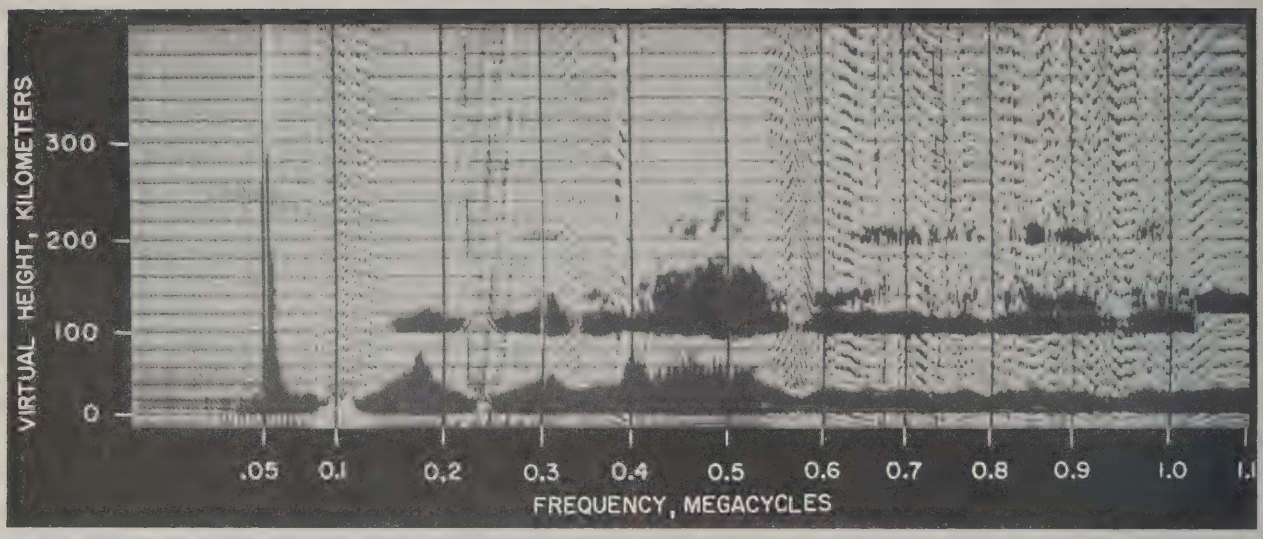


Effect of irradiation with different-colored light on the absorption spectrum of the dye, 4-dimethylamino azobenzene, in benzene solution. The dashed line represents the spectrum obtained when the solution is irradiated with green light while the dotted line shows results upon irradiation with blue light. Upon removal of the illumination, immediate reversal to the absorption spectrum represented by the solid line occurs.

It is interesting to note that azo dyes containing hydroxy groups adjacent to the azo group show little tendency to phototropism, probably because hydrogen bonding stabilizes the *trans* configuration. This is also true of thioindigo dyes dissolved in sulfuric acid, a solvent that can readily donate hydrogen ions to the solute, and of indigo dyes dissolved in organic solvents. In both these instances it is possible for the *trans* configuration to be stabilized by hydrogen bonding.

These results may also be applicable to solutions of dyes in glasslike solids, such as dyed plastics. Thus, it would seem that dyes having improved resistance to the effects of light might be obtained by synthesizing molecular structures with hydroxy or certain other hydrogen-containing groups in strategic locations, so as to provide a more rigid chemical structure through hydrogen bridging. Extension of the NBS study to include dyed fibers and the irreversible fading of dyes should provide information applicable to the more general problem of the light-fastness of all types of dyed fabrics.

For further technical details, see Cis-trans isomerism in thioindigo dyes, *by George M. Wyman and Wallace R. Brode, J. Am. Chem. Soc.* **73,** *1487 (1951)*; Absorption spectra of thioindigo dyes in benzene and chloroform, *by Wallace R. Brode and George M. Wyman, J. Research NBS* **47,** *170 (1951) RP 2241*; Absorption spectra of some thioindigo dyes in sulfuric acid, *by Wallace R. Brode and George M. Wyman, J. Am. Chem. Soc.* **73,** *4267 (1951)*; A shutter-illumination device for the study of phototropic dyes, *by John H. Gould and Wallace R. Brode, J. Opt. Soc. Am.* **42,** *380 (1952)*; Phototropism and *cis-trans* isomerism in aromatic azo compounds, *by Wallace R. Brode, John H. Gould, and George M. Wyman, J. Am. Chem. Soc.* **74,** *4641 (1952)*; Effect of solvent and of temperature on the *cis-trans* isomerization of azo dyes, *by Wallace R. Brode, John H. Gould, and George M. Wyman, J. Am. Chem. Soc.* **75,** *in press (1953)*.



Typical record of virtual height in kilometers versus frequency in megacycles of ionosphere reflections obtained by a low frequency recorder developed by the Bureau. Signals reflected from the ionosphere are recorded on a strip of moving film synchronized to the changes in frequency of the recorder (from 50 to 1100 kc). The black region at the bottom of the record is caused by the transmitter signals (not reflected from the ionosphere). The dark region at a height of about 100 kilometers is a display of the reflections from the ionospheric E region. A second layer in this region is shown by the dark areas at about 120 kilometers. The "herringbone" pattern is caused by interference from transmitting stations operating in the same frequency range. Especially noticeable is the interference set up in the broadcast band (from 550 kc).

A LOW-FREQUENCY IONOSPHERE RECORDER

As AN outgrowth of the increased interest and demand for more information concerning low-frequency radio propagation phenomena, the Bureau has developed a low-frequency recorder to probe the ionosphere. The recorder, developed by J. M. Watts, J. N. Brown, and J. C. Blair of the Bureau's central radio propagation laboratory, utilizes many of the principles incorporated in high-frequency recording equipment. Its operating frequencies of 50 to 1,100 kc are produced by use of the beat frequency method of generating wide frequency sweeps. Wide-band transmitter amplifiers, which utilize transformers containing ferromagnetic cores, deliver over 200 kw of pulsed power; but because of practical limitations an inefficient antenna system is used.

Since the early days of radio the communications industry has been expanding into higher and higher frequencies; as a result, interest in the low frequencies has lagged until recently. Consequently, little information now exists as to ionospheric phenomena below 1 megacycle. However, proposals for new kinds of radio navigation and location systems using both pulse and phase measuring schemes have focused renewed attention on additional applications of the lower frequencies. Further interest has been added also by the possibility of greater reliability at these frequencies.

One of the major obstacles to the full utilization of the lower frequencies was the lack of a transmitting system of sufficiently high power to generate pulsed signals over long distances. Early in 1950, NBS completed a low-frequency pulse transmitter which was experimentally operated on a fixed-frequency basis. The transmitter was a master oscillator-power amplifier type capable of delivering 100-microsecond pulses of over 1.5-kilowatt power. Vertical incidence reflections from the ionosphere were obtained at 37 kc; this is believed to be the first successful experiment of its kind at this frequency. The experimental results for 37, 50, 100, and 160 kc, however, were not of sufficient value to describe adequately the relation between apparent reflection height and frequency, which is one of the important parameters used in ionospheric analysis.

The complicated structure exhibited at times by the ionosphere recordings at 160 kc seemed to have some relation to the degree of geomagnetic activity, time of day, and frequency. Records made at 100 kc and below were generally less complicated. However, because the recorded variations from day to day were large and the characteristics often complicated, the single-frequency experiments strongly indicated the need for sweep-frequency type of exploration.

The principles first used in 1946 by P. G. Sulzer,[1] now of NBS, for high-frequency ionosphere recorders were adapted for use in the low-frequency model. The transmitter consists of six stages of wide-band amplification (four type-527 tubes are used in the output

Block diagram of low-frequency recorder developed to probe the ionosphere. The operating frequencies of the recorder (50 to 1100 kc) are produced by using the beat frequency method of generating wide frequency sweeps. Wide band transmitter amplifiers, which utilize transformers containing ferromagnetic cores, deliver over 200 kilowatts of pulsed power.

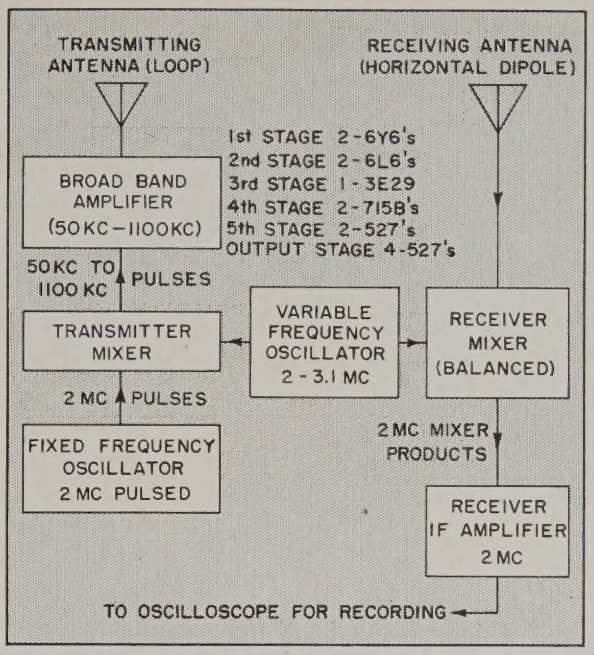
stage) fed by the output of a mixer. The mixer produces the difference frequency between two oscillators, one a continuous-wave oscillator variable in frequency from 2 Mc to 3.1 Mc, the other a pulsed oscillator at a fixed frequency of 2 Mc. The variable-frequency oscillator is used as the converter in the mixer of the receiver so that reflected pulses are automatically converted to 2 Mc, the intermediate frequency of the receiver.

The band width of the low-frequency transmitter amplifier is about 1 Mc, reducing the technical complications as compared to the required 25-Mc bandwidth for the high frequency recorder. Also, the low frequency permits the use of ferromagnetic cores in all transmitter stages. As a result, push-pull operation with appreciable inductive coupling between the plate circuits is possible, which allows the high-power stages to operate Class B with a reasonably good waveform.

Adjustments for flatness of over-all transmitter response were made with a dummy load of 500 ohms. Because the recorder contains six stages of amplification, identical frequency response characteristics in each stage would produce an over-all response of greatly exaggerated unevenness. Consequently, each stage is adjusted separately while the over-all response is observed at the driver stage output. The output of the mixer is fed into a low-pass filter that includes a terminating resistance across the primary of a transformer coupling the filter to the first push-pull amplifier stage. The resistance is adjusted to mismatch the filter and causes a peak in its output at the cutoff frequency (1 Mc); the size of the peak is adjusted by variation of the resistance. By this means alone, the power output of the driver stage is made slightly greater at the high-frequency end than in the midfrequency range.

The plate circuit of the push-pull amplifier contains an R-C parallel circuit, the capacitor of which is large enough to tune out the primary self-inductance of the transformer at approximately 50 kc. The resistance inserted in series with this capacitor reduces the resonant circuit Q to approximately 2. Another resistance in parallel with the transformer primary provides a small additional loss at all frequencies that improves the waveform delivered to the beam power tubes in the final stage.

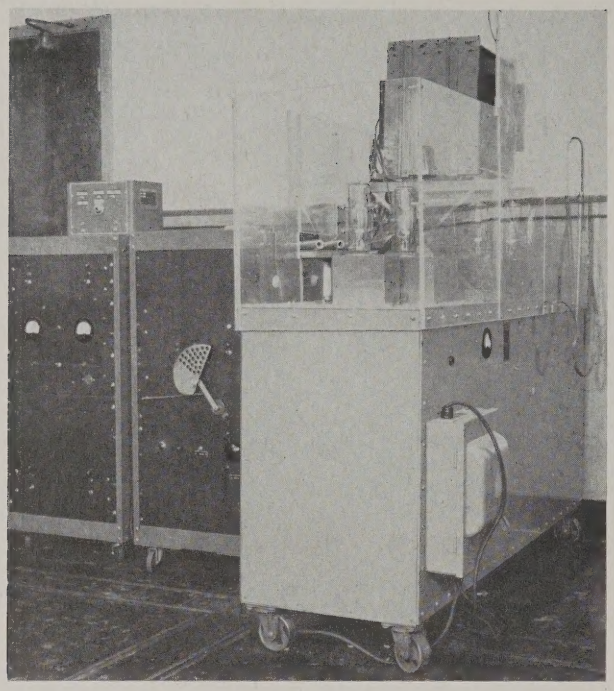
Equalization in all stages produces a response that is reasonably flat from 50 kc to 1 Mc measured at the grids of the final amplifier. The power delivered by the final amplifier into a 500-ohm resistive load averages about 1.5 megawatts up to 500 kc and then drops to about 0.5 megawatt for the remainder of the frequency range.



A single loop antenna is used to radiate the energy in a vertical direction. It is suspended between two vertical supports approximately 350 ft long and about 150 ft high. Although a single long-line antenna would perform more efficiently throughout the entire frequency range, a required length of about 9,830 ft makes its use prohibitive. In fact, in all low frequency applications the efficiency of the antenna system must be seriously compromised in order to achieve realizable physical dimensions. Because the transmissions must be vertically directed, rhombics and V-types cannot be utilized. Furthermore, the use of a delta antenna would require a structure several thousand feet high. Measurement of the peak-pulse current of the loop antenna at 100 kc indicates that the radiated power is of the order of 5 w. In spite of this low value, reflections are frequently recorded at 100 kc during the night hours.

The record of apparent reflection height of the ionosphere layers versus frequency is made by intensity-modulation of an oscilloscope beam to which a line deflection type of time base is applied. The line produced is photographed by a camera with film moving in synchronism with the frequency-change motor of the transmitter and in a direction of travel perpendicular to the time base line. Pips from a 7,500-cycle oscillator form on the film horizontal markers which represent 20-kilometer intervals in apparent height. The direct pulses from the transmitter form an uneven trace at the bottom of the film. Frequency marks at 100-kc intervals, produced by a cam-operated microswitch at the frequency changing mechanism, show as vertical lines on the film. The received signals appear on the film as broad traces at the height from which they were reflected.

The fact that low-frequency transmitting stations, which are the chief sources of interference, almost



Frequency generating and amplifying equipment used in the low-frequency recorder. The rack at the left contains the mixing equipment for producing a difference frequency between two oscillators. The two oscillators, one a continuously variable from 2 to 3.1 Mc, the other a pulsed oscillator at a fixed frequency of 2 Mc, are contained in the next rack to the right. The cam that automatically changes the variable oscillator is mounted on the front of this rack. The final amplifiers are located in the plastic-enclosed unit at the right.

always use vertically polarized antennas has been utilized in the design of the receiving antenna. The antenna is a low, horizontal dipole which is very effective for receiving downcoming signals but which has low sensitivity to the nearly vertically polarized interfering signals. Despite these advantages, the effective sensitivity of the receiver is lowered greatly at some frequencies by interfering stations close by. The standard broadcast band, beginning at 550 kc, causes some trouble but not as much as might be anticipated.

The records obtained in the low-frequency experiments show a diurnal variation. Reflections from the ionospheric E region are apparent at about 100 kilometers above the transmitter. The extraordinary component of the F layer and the ordinary component appear only at night. Occasionally, there appears at night between the E and F layer another trace or group of traces which seems very similar to what have been called E_2-layer traces when observed on the conventional daytime high-frequency ionosphere record.

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[1] *P. G. Sulzer,* Ionosphere measuring equipment, *Electronics, July 1946.*

Heat Generation in the Hardening of Magnesite Cements

A RECENT STUDY by the Bureau provides the first published figures on the amount of heat generated in the setting of magnesium oxychloride cements, also known as magnesite cements or Sorel cements. Formed by the action of concentrated magnesium chloride solution on active magnesium oxide, these cements are extensively used, especially for floors. They generate much more heat in the process of hardening than does portland cement, and this might cause serious difficulty under some circumstances; the heat evolved by a large mass of magnesium oxychloride cement could easily raise temperatures to well above the boiling point of water.

In the NBS investigation, which was conducted by E. S. Newman, J. V. Gilfrich, and L. S. Wells of the Bureau's mineral products laboratories, nine representative commercial magnesite cements were studied. Investigated in addition to the commercial cements—which contain various desirable inert materials such as asbestos fiber, hardwood sawdust, talc, sand, and powdered silica—were some laboratory-mixed pastes consisting only of magnesium oxide (MgO), magnesium chloride ($MgCl_2$), and water, in various proportions. For the commercial cements, heat generated during the first 18 hours of hardening (during which time heat generation is substantially complete) was found to be about 190 calories per gram of magnesium oxide (MgO). For the laboratory pastes of various proportions, NBS obtained a wide range of heat-of-hardening values, from 135 to 320 cal/g of magnesium oxide. The low heats of hardening measured for some of these pastes support the conclusion of previous investigators that free MgO may remain in such pastes.

Magnesite cements have been known and used to some extent for many years. Electrically conducting, they are particularly valuable for making nonsparking floors in plants that manufacture explosives and in the operating rooms of hospitals. Other applications include floors for office buildings, stores, ships, and railroad passenger cars. Because they absorb neutrons more effectively than do portland cements, they have recently been proposed for the heavy protective walls needed in some phases of atomic energy work.

Although it seems well established that magnesite cements can give excellent service in some applications, some users have reported disappointing results. The mechanisms of the difficulties that have arisen are not well understood, but it is likely that some instances of unsatisfactory performance have resulted from nonuniform methods of preparation and application. No

generally accepted standard specifications for preparation and application of these cements have yet been adopted.

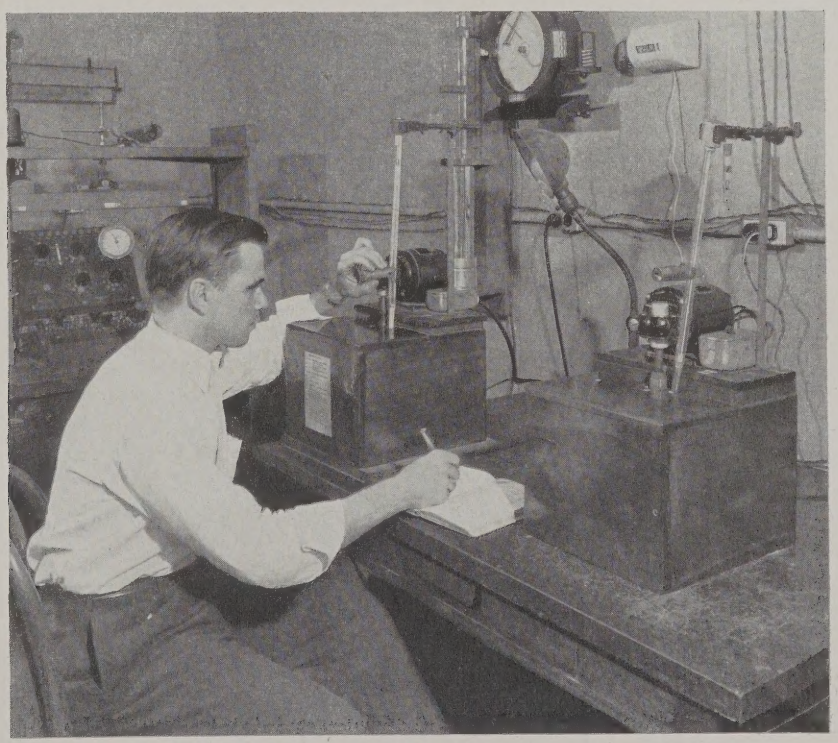
With the end of World War II, a large amount of productive capacity that had been devoted to making metallic magnesium for aircraft applications became available for other uses, including manufacture of the ingredients of magnesite cements. The increased importance of these cements has led to the establishment of an ASTM (American Society for Testing Materials) committee, headed by the Bureau's Dr. L. S. Wells, that is engaged in preparing ASTM specifications both for the composition and for the application of the cements. Cooperating in this work, the Bureau undertook the present investigation of heats of hardening.

Three different calorimetric procedures were used in the NBS study. The heats of hardening of the laboratory pastes—which contained no inert or filler material—were determined indirectly by a heat-of-solution method similar to that used for portland cement. In this procedure, the heat of solution of a sample of the hardened paste was determined in hydrochloric acid (2.00 normal). Also determined, by use of similar HCl solutions, where the heat of solution of the magnesia and the heat of dilution of the magnesium chloride solution used in preparation of the paste. The difference between the properly weighted sum of these last two values and the heat of solution of the hardened sample is the heat evolved during the hardening of the paste.

This indirect heat-of-solution method that was used for the laboratory pastes requires that the materials be soluble in the acid and that the paste be analyzed chemically. In determination of the heats of hardening of the commercial cements two direct methods were used. In the first of these methods, cement samples were allowed to harden in corked vacuum flasks while their internal temperatures were recorded. Electrical calibration of the flasks permitted the heat evolved by the cement to be calculated from the recorded temperatures.

Because the cements in the vacuum flasks reached temperatures as high as 100° C, a second set of direct measurements was made in a Lerch conduction calorimeter. In this apparatus the heat generated by the cement flows over a calibrated path into a water bath at constant temperature. Because of the more rapid flow of heat from the specimen the Lerch equipment permits the cement to harden at lower temperatures than those at which the cement hardens in the vacuum flasks; the temperatures reached by the cement in this instrument were only a few degrees above the temperature of the room. The path of heat flow was a brass tube, one end of which was in contact with the cement and the other end of which was maintained at the temperature of the water bath. Resistance thermometers attached to the tube permitted the temperature drop along the tube to be recorded. From recorded temperature differences and from electrical calibration of the instrument it was possible to calculate the amount of heat evolved by the cements.

For further technical details, see Heat generation in the hardening of magnesium oxychloride cements, *by E. S. Newman, J. V. Gilfrich, and L. S. Wells, J. Research NBS* **49**, *377 (Dec. 1952); reprinted as NBS Research Paper 2375, obtainable for 10 cents from Superintendent of Documents, Government Printing Office, Washington 25, D. C.*



Making a temperature reading on a heat-of-solution calorimeter at the Bureau. The thermometer being read extends into a Dewar flask (inside the box) containing the cement sample, which is being dissolved in hydrochloric acid. The flask has been calibrated electrically, so that the heat of solution can be calculated from the temperature.

Publications of the National Bureau of Standards

Periodicals

Journal of Research of the National Bureau of Standards, volume **50,** number 3, March 1953 (RP2399 to RP2406 incl.). Annual subscription, $5.50.

Technical News Bulletin, volume **37,** number 3, March 1953, 10 cents. Annual subscription, $1.00.

CRPL–D103. Basic Radio Propagation Predictions for June 1953. Three months in advance. Issued March 1953, 10 cents. Annual subscription, $1.00.

Research Papers

Reprints from Journal of Research, volume **50,** *No. 2, February 1953.*

RP2389. Beryllium-uranium system. R. W. Buzzard. 10 cents.

RP2390. Pulsed light system for multiple-cell ultracentrifuge rotor. M. Wales, P. G. Sulzer, and L. C. Williams. 5 cents.

RP2391. Damping of elastically supported element in a vacuum tube. S. Levy, E. V. Hobbs, W. D. Kroll, and L. Mordfin. 5 cents.

RP2392. Calormetric determination of the half-life of polonium. D. C. Ginnings, Anne F. Ball, and D. T. Vier. 10 cents.

RP2393. Determination of molecular weights of dextrans by means of alkaline copper reagents. H. S. Isbell, C. F. Snyder, N. B. Holt, and M. R. Dryden. 10 cents.

RP2394. An interferometer procedure applied to the study of the chemical durability of silicates, enamels, and metals. Robert G. Pike and Donald Hubbard. 10 cents.

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RP2396. Hydrodynamic effects of gales on Lake Erie. Garbis H. Keulegan. 15 cents.

RP2397. Twisted square plate method and other methods for determining the shear stress-strain relation of flat sheet. Walter Ramberg and James A. Miller. 15 cents.

RP2398. Stress-strain relation in shear from twisting test of annulus. Walter Ramberg and James A. Miller. 10 cents.

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M207. Annual report 1952 National Bureau of Standards. 30 cents.

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Applied Mathematics Series

AMS24. Introduction to the theory of stochastic processes depending on a continuous parameter. Henry B. Mann. 30 cents.

AMS28. Tables of Bessel-Clifford functions of orders zero and one. 45 cents.

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Thermodynamic properties of gaseous difluorodichloromethane (Freon–12). Joseph F. Masi. J. Am. Chem. Soc. (1155 Sixteenth Street, NW., Washington 6, D. C.) **74,** 4738 (1952).

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